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Performance of mesoporous ZSM-5 in deoxygenation of straw derived pyrolysis vapors

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1. Introduction

In order to allow processing of biomass derived fast pyrolysis oils in oil refineries, reduction of the oil's oxygen content and acid number is required [1]. Deoxygenation can be obtained by direct upgrading of the pyrolysis vapors over solid acid catalysts. A close coupled process operating at temperature and pressure conditions close to those for optimum liquid yields in pyrolysis units offers potential economic advantages over high pressure hydrotreating [2]. To date, the medium pore size ZSM-5 zeolite provides a high aromatic yield and the least amount of coke in upgrading of pyrolysis vapors [3]. However, the coke caused by reactive pyrolysis vapors causes a rapid decay in site accessibility and requires frequent regeneration to recover activity. In addition, irreversible dealumination can be caused by steam from the pyrolysis process, the dehydration reactions during upgrading and the steam produced during oxidative regeneration. We address the reversible deactivation due to coke by introducing an auxiliary mesopores network to improve the accessibility and prolong the zeolite's active time on stream. In order to reduce the irreversible deactivation, the zeolites acid site strength and density have been balanced with modifications by phosphorous stabilization.

2. Experimental

The screening of the parent, mesoporous, and phosphorous modified ZSM-5 zeolites was performed with 20 -150 g of catalyst in a fixed bed reactor downstream an ablative type pyrolysis unit. Prior to upgrading the zeolite was steamed to achieve accelerated dealumination. Crushed wheat straw pellets were used as feedstock at a feeding rate of ~2g/min. By varying the runtime and amount of catalyst, a wide range of biomass feed to catalyst (B:C) ratios was covered and upgraded liquid product was collected at an optimized condensation train, followed by detailed analysis of the liquids in terms of moisture, elemental analysis, size exclusion chromatography (SEC) and quantification of ~200 components by GC-MS/FID. Catalyst characterization was performed with ICP/XRF, NH₃-TPD, N₂ and Ar-physisorption, TEM and XRD.

3. Results and discussion

Mass and energy balances > 90 % were obtained. Towards higher B:C values, the obtained oils consist both of fully upgraded products when the catalyst was fresh and products from the breakthrough of primary pyrolysis vapors. In order to unravel the change in oil-quality with increased B:C ratio, a series of successive biomass conversion steps was performed. Towards higher B:C values, a decreasing yield of monoaromatics is accompanied by a decreased selectivity to BTX products (Fig. 1a). At 500°C, all zeolites clearly reduced the oxygen content of the oil with respect to oil obtained from passing the vapors over a silicon carbide bed (Fig. 1b). The benefit of an auxiliary mesopore network becomes apparent for oils collected at higher B:C ratios: While the microporous ZSM-5 rapidly loses its deoxygenation ability (see CBV30 for Σ B:C 0.6 to 2.6), the mesoporous ZSM-5 maintains a similar degree of deoxygenation for almost four times higher B:C ratio (see CBV30 for Σ B:C 4 to 10.2). While phosphorous stabilized mesoporous CBV55 achieves less deoxygenation at the low B:C range, their deoxygenation performance at higher B:C of ~9 is still comparable to the microporous counterpart at lower B:C of ~6. We further find that the introduction of mesopores results in higher coke formation, which can be mitigated by the addition of phosphorous.

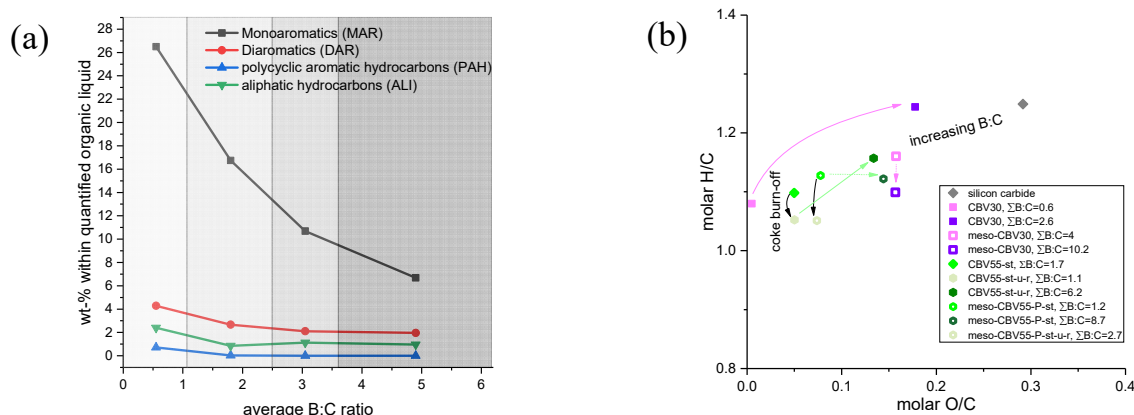


Figure 1: (a) Change of deoxygenated liquid products with increasing catalyst deactivation by coke, here shown for steamed CBV55 (b) Performance of micro and mesoporous ZSM-5 at operating temperature of 500°C based on molar H/C and O/C ratio; “P”, “st”, “u”, and “r” refers to phosphorous modification, steaming, use, and oxidative regeneration, respectively

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